

Homochiral self-sorted and emissive Ir(III) metallo-cryptophanes

Victoria E. Pritchard,^[a] Diego Rota Martir,^[b] Samuel Oldknow,^[a] Shumpei Kai,^[c] Shuichi Hiraoka,^[c] Nikki J. Cookson,^[a] Eli Zysman-Colman*,^[b] and Michael J. Hardie*,^[a]

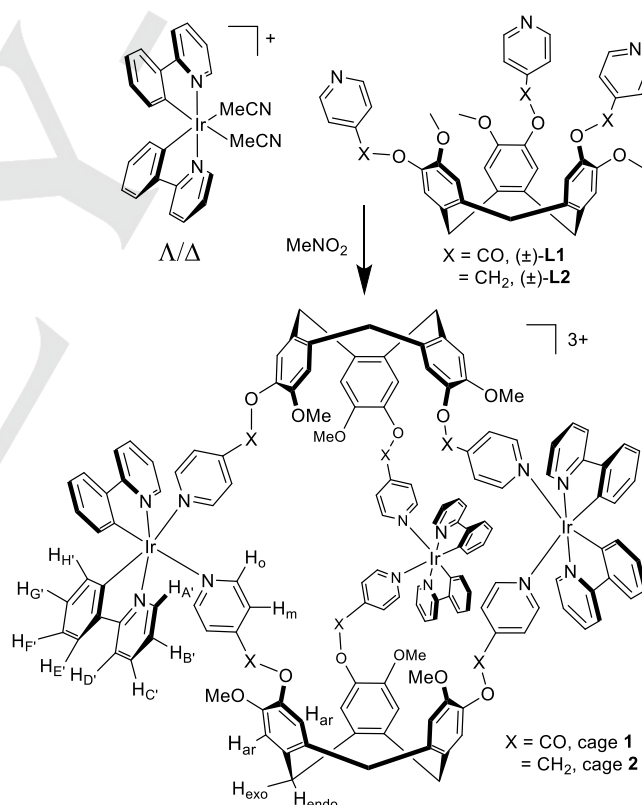
Dedicated to the memory of Dr Julie Fisher.

Abstract: The racemic ligands (\pm)-*tris*(isonicotinoyl)-cyclotriguiacylene (L1), or (\pm)-*tris*(4-pyridyl-methyl)-cyclotriguiacylene (L2) assemble with racemic (Λ, Δ)-[Ir(ppy)₂(MeCN)₂]⁺ where ppy = 2-phenylpyridinato to form [Ir(ppy)₂]₃(L)₂³⁺ metallo-cryptophane cages. The crystal structure of [Ir(ppy)₂]₃(L1)₂·3BF₄ has *MM*- $\Lambda\Lambda\Lambda$ and *PP*- $\Delta\Delta\Delta$ isomers, and homochiral self-sorting occurs in solution, a process accelerated by a chiral guest. Self-recognition between L1 and L2 within cages does not occur, and cages show very slow ligand-exchange. Both cages are phosphorescent, with [Ir(ppy)₂]₃(L2)₂³⁺ having enhanced and blue-shifted emission when compared with [Ir(ppy)₂]₃(L1)₂³⁺.

Metallo-cages are discrete 3-D coordination assemblies with a hollow interior with applications as hosts and nanoscale vessels.^[1] They form through the self-assembly of multidentate ligands with metals, or with metal complexes with controlled available coordination sites ("metallo-tectons"). Luminescent metallo-cages are known,^[2-6] with most examples exhibiting fluorescence-active ligands,^[2] alongside rarer examples of cages with pendant metal-complex emissive groups.^[3] There are very few examples of metallo-cages constructed from inherently phosphorescent structural components.^[4-6] Cyclometalated Ir(III) complexes bearing either two N-donor ligands or one N[^]N chelating ligand represent an important subclass of phosphorescent materials.^[7] Lusby et al reported the enantiopure Ir(III) metallo-cage [Ir(ppy)₂]₆(tcb)₄·(OTf)₆ (tcb = 1,3,5-tricyanobenzene)^[4] which self-assembles, despite the inertness of the d⁶ Ir(III) center, as the *C, C-cis-N, N-trans* arrangement of the ppy ligands has a *trans* labilising effect. The cage shows red-shifted emission compared with a monomeric analogue, and enhanced photoluminescence quantum yields (Φ_{PL}). To date, this is the only report of a 3-D

metallo-cage that utilizes [Ir(ppy)₂] as the sole metal centre, although mixed metal examples are known.^[5]

We report herein two metallo-cages of the type [Ir(ppy)₂]₃(L)₂³⁺ where L is a chiral tripodal ligand related to the molecular host cyclotrimeratrylene (CTV). {M(chelate)}₃L₂ cages with CTV-type ligands are known as metallo-cryptophanes, and most examples feature square planar metals.^[8] The [Ir(ppy)₂]₃(L)₂³⁺ cages reported here show homochiral sorting on crystallization and in solution, and slow ligand exchange behavior is observed.



Scheme 1. Synthesis of metallo-cryptophane cage species.

Cages [Ir(ppy)₂]₃(L1)₂³⁺ **1** and [Ir(ppy)₂]₃(L2)₂³⁺ **2** are formed from nitromethane mixtures of (Λ, Δ)-[Ir(ppy)₂(MeCN)₂]⁺·X (X = PF₆⁻, BF₄⁻) and (\pm)-L1 or (\pm)-L2 in 3:2 stoichiometry, Scheme 1. Electrospray ionization mass spectrometry (ESI-MS) gives a triply charged *m/z* peak at 983.1120 (cage 1) or at 955.2853 (cage 2), along with [Ir(ppy)₂]₃(L)₂³⁺ and [Ir(ppy)₂]₂(L)₂³⁺ fragment species (SI Figs. S3, S4). Initial ¹H NMR of [Ir(ppy)₂(NCMe)₂]⁺·X and L in d₃-MeNO₂ show considerable broadening of the resonances and chemical shift changes, most saliently the ppy protons *ortho* to the coordinating N (H_{Ar}) and C (H_H) move upfield

[a] Dr V. E. Pritchard, S. Oldknow, Dr N. J. Cookson, Prof. M. J. Hardie
School of Chemistry
University of Leeds
Woodhouse Lane, Leeds LS2 9JT, UK
E-mail: m.j.hardie@leeds.ac.uk

[b] D. Rota Martir, Dr E. Zysman-Colman
Organic Semiconductor Centre, EaSTCHEM School of Chemistry
University of St Andrews
St Andrews, Fife KY16 9ST, UK
E-mail: eli.zysman-colman@st-andrews.ac.uk

[c] S. Kai, Prof S. Hiraoka
Department of Basic Science
Graduate School of Arts and Sciences
The University of Tokyo
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

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and downfield, respectively, and for cage **2** the previously sharp CH₂ bridge singlet of L2 at 5.19 ppm becomes a complex multiplet as free rotation is hindered (Fig. S15). ROESY spectra of **1** and **2** give expected couplings, including between H_{H'} on the ppy's and the *ortho* pyridyl protons of L (Figs. S8, S16). Diffusion ordered NMR in *d*₃-MeNO₂ for **1**·3PF₆ (Fig. S9) gave a hydrodynamic radius of 18.99 Å.

The structure of **1**·3BF₄·*n*(MeNO₂) was confirmed by crystallography, Fig. 1.^[9] There are two independent cage **1** cations that show minor structural differences. Anions and additional solvent were not located due to significant disorder. Each cage has three pseudo-octahedrally coordinated Ir(III) centers, each with two ppy ligands and the pyridyl groups from two L1 ligands in a *cis* arrangement. The two L1 ligands bridge between three Ir(III) centers. Average torsion angle between *cis* pyridyl groups is 38.04°, typical for [Ir(ppy)₂(pyridyl)₂]-type complexes^[10] with the bowl shape of CTV-type ligands able to accommodate these torsion angles within the cage structure.

Both L1 ligands within each cage **1** are the same enantiomer, giving the chiral *anti*-cryptophane isomer. Each [Ir(ppy)₂]⁺ unit within a cage has the same chirality, such that only the enantiomeric *MM*- $\Delta\Delta\Delta$ and *PP*- $\Delta\Delta\Delta$ cage isomers are observed in the structure. Given the Δ and Λ enantiomers of the [Ir(ppy)₂]⁺ moieties and the *M* and *P* enantiomers of the L-types ligands are present in the reaction mixture, there are twelve possible stereoisomers of the cage.

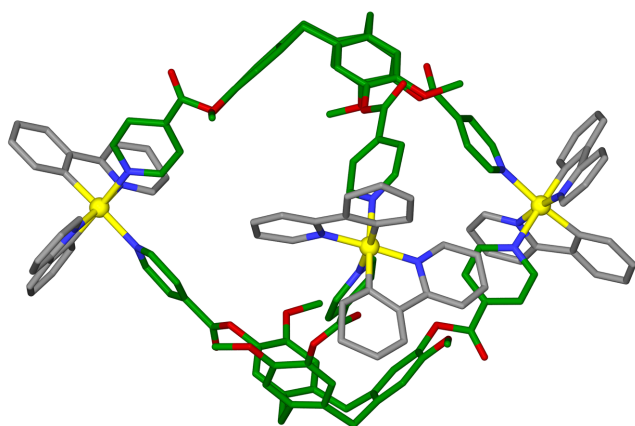


Figure 1. A $\{[\text{Ir}(\text{ppy})_2(\text{L}1)_2]^+\}$ cage from the crystal structure of **1**·3BF₄·*n*(CH₃NO₂), L1 and ppy ligands shown in green and grey respectively.

The ¹H NMR spectra of both cages **1** and **2** undergo significant sharpening upon standing (Figs. S7 and S15), and fully equilibrate after several months. The ¹H NMR spectrum of cage **1**·3PF₆ collected after 3 months of standing is virtually identical to that of the single crystals of **1**·3BF₄·*n*(CH₃NO₂) re-dissolved in *d*₃-MeNO₂, Fig. 2a/b. (±)-L1 was resolved into its constituent enantiomers by chiral HPLC,^[11] and each L1 enantiomer reacted with each of Δ -[Ir(ppy)₂(MeCN)₂]-BF₄ and Λ -[Ir(ppy)₂(MeCN)₂]-BF₄. As expected, two combinations were mis-matched pairs of enantiomers that gave poorly resolved ¹H NMR spectra (Figs. S10–11) while two combinations were matched pairs (presumably *M*- Δ and *P*- Λ) gave sharp spectra in short timeframes that were similar to the fully sorted cage mixture (Figs. 2d, S12–13). ESI-MS of matched and mis-matched pairs are similar with all combinations showing cage formation (Fig. S14). The observed ¹H NMR spectral sharpening is therefore indicative of equilibration

involving chiral self-sorting of an initial mixture of cage stereoisomers, as was also seen in our previous studies of a [Pd₆(L1)₆]¹²⁺ cage but where only the ligand was a chiral component.^[12] We could not resolve the sorted cages by analytical chiral HPLC.

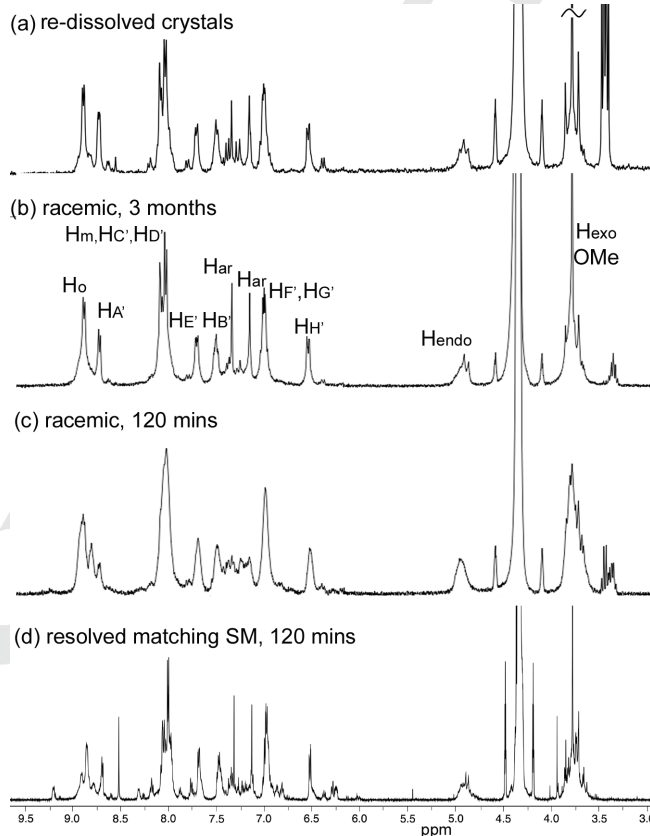


Figure 2. ¹H NMR spectra of cage **1** in CD₃NO₂ of (a) re-dissolved racemic single crystals of *MM*- $\Delta\Delta\Delta$ and *PP*- $\Delta\Delta\Delta$ cages of **1**·3BF₄; (b) (Δ , Δ)-[Ir(ppy)₂(MeCN)₂]-PF₆ and (±)-L1 3 months after mixing; (c) (Δ , Δ)-[Ir(ppy)₂(MeCN)₂]-PF₆ and (±)-L1 two hours after mixing; (d) matched pair of Δ -[Ir(ppy)₂(MeCN)₂]⁺ and one L1 enantiomer after 2 hrs.

Homochiral metallo-cages with *tris*-chelate metal coordination are known both from achiral^[13a–b] and resolved chiral ligands.^[13c–e] Metallo-cages that show homochiral self-sorting from a racemic mixture of ligand enantiomers observed in solution are rare,^[14] though include Pd(II) metallo-cryptophanes.^[8a] The simultaneous chiral self-sorting of both ligand and pre-formed inert metallo-tecton as reported here has not been previously reported.

In a preliminary investigation of the influence of chiral guests on the self-assembly of cage **1** globular additives were included in 3:2 mixtures of (Δ , Δ)-[Ir(ppy)₂(MeCN)₂]-PF₆ and (±)-L1. Addition of chiral *R*-camphor or *S*-camphor led to noticeably faster sharpening of the ¹H NMR spectra than in their absence, but this was not observed for addition of achiral adamantane (Fig. S15–S20). Interestingly, addition of the related anionic species *R*-(or *S*)-10-camphorsulfonic acid to the reaction mixture prevents cage formation presumably as carboxylate is a competing ligand for the iridium (Fig. S21–22).

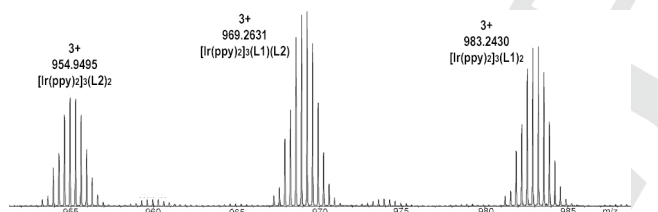
The cages do not show self-recognition of L-ligand species. ESI-MS of a MeNO₂ solution of L1, L2 and [Ir(ppy)₂(MeCN)₂]-BF₄

Table 1. Photophysical properties of complexes **1**:3(BF₄) and **2**:3(BF₄).

	λ_{em} (nm)			$\Phi_{PL}(\%)^{[d]}$			τ_e (ns) ^[g]		
	DCM [a,b,f]	film [c,f]	powder	DCM [a]	Film [c,e]	powd er [e]	DCM [a]	film [c]	powder
1	604	481 (0.7), 514 (1), 556 (0.8)	648	1	5.5	1.3	59 (0.7), 129 (0.3)	634 (0.4), 2319 (0.6)	55 (0.6), 203 (0.4)
2	485 (0.8), 516 (1), 547 (0.6)	486 (0.8), 515 (1), 545 (0.6)	519	15	10	1.6	523 (0.4), 887 (0.6)	688 (0.7), 3042 (0.3)	141 (0.4), 1175 (0.6)

[a] Measurements in degassed DCM at 298 K. [b] Quinine sulfate employed as the external reference ($\Phi_{PL} = 54.6\%$ in 0.5 M H₂SO₄ at 298 K). [c] PMMA doped films (5 wt % of cage) formed by spin-coating deposition on quartz substrate. [d] Φ_{PL} measurements were carried out under nitrogen ($\lambda_{exc} = 360$ nm). [e] values obtained using an integrating sphere. [f] Principal emission peaks listed with values in brackets indicating relative intensity. [g] $\lambda_{exc} = 378$ nm; Values in parentheses are pre-exponential weighting factor, in relative % intensity, of the emission decay kinetics.

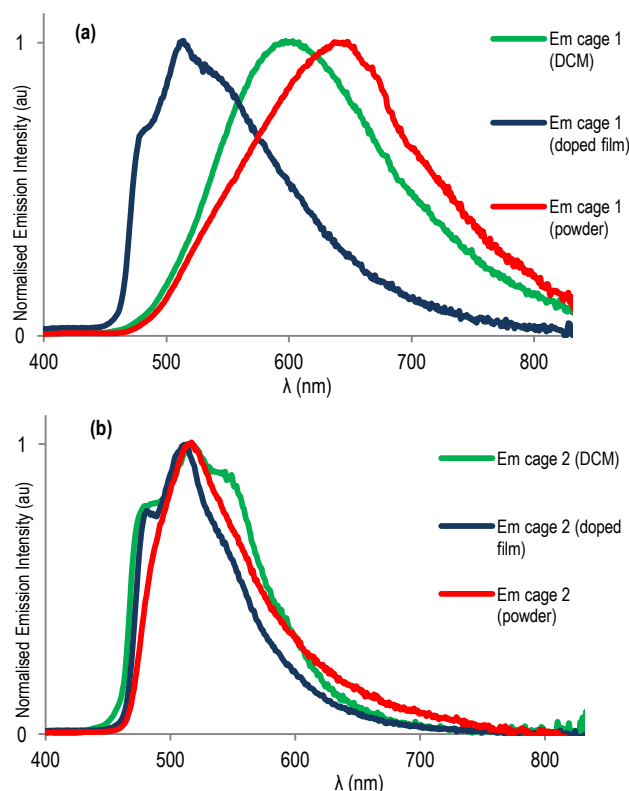
shows a statistical mixture of **1**: $[\text{Ir}(\text{ppy})_2]_3(\text{L1})(\text{L2})^{3+}$:**2** cage species, Fig. 3. Mixing **1**:3BF₄ and **2**:3BF₄ in MeNO₂ results in very slow exchange between L1 and L2 with appreciable ligand exchange only observed after 4 weeks, and near-statistical mixing reached after 10 weeks (Figure S6). Thus these cages have a high degree of kinetic stability but are not completely inert. It is interesting to note that this speciation behavior is in contrast with recently reported $[\text{Pd}_3\text{L}_2]^{6+}$ metallo-cryptophanes, which exclusively formed homocages from two different L-type ligands, with no ligand exchange.^[8a]

**Figure 3.** ESI-MS of a 1:1:3 mixture of L1:L2: $[\text{Ir}(\text{ppy})_2(\text{MeCN})_2]\cdot\text{BF}_4$ in MeNO₂ showing formation of statistical mixture of homoleptic and heteroleptic cages.

The absorption spectra of **1** and **2** in dichloromethane (DCM) are similar to other $[\text{Ir}(\text{ppy})_2(\text{N}^*\text{N})]^+$ systems,^[7] and characterised by two intense ligand centered (¹LC) transitions between 260 and 320 nm localised on the ppy and three lower intensity broad bands at below 380 nm that consist of spin-allowed and spin-forbidden mixed metal-to-ligand and ligand-to-ligand charge transfer (¹MLCT/¹LLCT and ³MLCT/³LLCT) transitions (Fig. S26). The weak CT transition observed for **1** at 470 nm was not reported for the monomeric $[\text{Ir}(\text{ppy})_2(4\text{-pyCO}_2\text{Et})_2]^+$ (4-pyCO₂Et = 4-ethyl isonicotinate),^[10c] pointing to increased conjugation in **1** due to the CTV scaffold. For both **1** and **2**, the excitation spectra in DCM match the absorption spectra and indicate a single photophysically-active species.

Cages **1** and **2** are emissive in DCM solution and in the solid state. Upon photoexcitation of **1**, a broad and unstructured emission is observed both in DCM and in the powder, Fig. 4a, due to emission from a mixed ³MLCT/³LLCT state.^[7] The photoluminescence spectrum in the powder is red-shifted ($\lambda_{max} = 648$ nm) compared to that in DCM ($\lambda_{max} = 604$ nm); however, **1** possesses similarly low Φ_{PL} of around 1% and bi-exponential decay kinetics in both media, Table 1. Due to the increased conjugation into the CTV scaffold, cage **1** shows red-shifted emission and similar Φ_{PL} compared to $[\text{Ir}(\text{ppy})_2(4\text{-pyCO}_2\text{Et})_2]^+$ ($\lambda_{max} = 560$ nm; $\Phi_{PL} = 2\%$).^[10c] Lusby's $[\text{Ir}(\text{ppy})_2]_6(\text{tcb})_4^{6+}$ cage also showed red-shifted emission ($\lambda_{max} = 575$ nm) when compared with the corresponding $[\text{Ir}(\text{ppy})_2(\text{NCPH})_2]\text{OTf}$ complex ($\lambda_{max} = 525$ nm); however, unlike for cage **1** and other $\text{Ir}(\text{ppy})_2$ discrete supramolecular systems,^[15] the Φ_{PL} for the Lusby cage was enhanced compared with that of the mononuclear complex ($\Phi_{PL} = 4\%$ cf. $\Phi_{PL} < 1\%$).^[4]

In order to mitigate non-radiative vibrational motion in the cage we spin-coated 5 wt % of **1** in polymethyl methacrylate (PMMA), which serves as an inert matrix. The emission in the thin film was blue-shifted and more structured ($\lambda_{max} = 514$ nm) compared to both the powder and solution spectra. The Φ_{PL} of 5.5% was enhanced as a result of the rigidification conferred by the PMMA host and the emission lifetimes were significantly longer ($\tau_e = 634$ and 2319 ns).

**Figure 4.** Normalised photoluminescence spectra of a) **1**:3BF₄ and b) **2**:3BF₄. Dotted lines de-aerated DCM solution; dashed lines PMMA doped films with 5 wt % of cages spin-coated on a quartz substrate; red lines bulk powders.

The photoluminescence spectrum of cage **2** in DCM is more structured and blue-shifted ($\lambda_{\text{max}} = 516 \text{ nm}$) compared to **1**, indicating emission that is more predominantly ligand-centered (^3LC) (Fig. 4(b)). The blue-shifted emission of **2** compared to **1** was expected considering the presence of the electron-withdrawing ester moieties located on L1 in **1**, which stabilise the LUMO.^[10c] Cage **2** shows a significantly enhanced Φ_{PL} and longer τ_e compared to **1** in DCM ($\Phi_{\text{PL}} = 15\%$, $\tau_e = 523, 887 \text{ ns}$).

Unlike for **1**, as a powder the emission of **2** is not significantly red-shifted ($\lambda_{\text{max}} = 519 \text{ nm}$) though the emission profile is less structured, showing less well-resolved vibrational bands as shoulders of the main emission peak. The emission profile for **2** in PMMA doped thin film is likewise very similar to that in DCM. Though Φ_{PL} values are low in the powder ($\Phi_{\text{PL}} = 1.6\%$), in doped film they are higher ($\Phi_{\text{PL}} = 10\%$). Emission lifetimes are expectedly longer in doped films than in powder, Table 1. Attempts to synthesize an analogous mononuclear complex of 4-phenoxyethylpyridine for comparison were not successful due to ligand oligomerization.

In summary, phosphorescent $[\{\text{Ir}(\text{ppy})_2\}_3(\text{L})_2]^{3+}$ metallocryptophanes can be synthesized in high yields, with the CTV-type ligands able to accommodate torsion angles typical of $[\text{Ir}(\text{ppy})_2(\text{L})_2]$ complexes to form rare examples of 3-D Ir(III) cyclometallated coordination cages. These cages undergo ligand exchange processes over months, and show a remarkably high degree of homochiral self-sorting of both ligand and metallocation, but not self-recognition between similar L-type ligands. Chiral sorting is enhanced by the presence of neutral chiral additives. For cage **1** chiral self-sorting occurs relatively rapidly upon crystallization through an induced seeding effect, but on a timescale of months in solution. Luminescence properties of the two cages are quite distinct, pointing to an ability to tune the photophysical properties of these systems. Cage **2** showed an enhanced and blue-shifted emission compared to **1**, reaching a Φ_{PL} of 15% in DCM solution and 10% in doped film. These are promising systems for a variety of applications: as semiochemical hosts, photoredox catalysts and in energy conversion materials.

Acknowledgements

We thank the EPSRC (DTG award 1238852, EP/K039202/1, EP/M02105X/1, EP/J001325/1), Leverhulme Trust (RPG-2014-148), University of St Andrews, and the MEXT/JSPS Grants in Aid for Scientific Research (JP25102005 and JP25102001) for funding; Simon Barrett for assistance with NMR; Martin Huscroft for assistance with HPLC, and Stephen Boyer for elemental analysis measurements.

Data accessibility. Data supporting this work can be accessed at DOI:#####.

Keywords: supramolecular chemistry; cage compounds • homochiral self-sorting • phosphorescence

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Victoria E. Pritchard, Diego Rota Martir,
Samuel Oldknow, Shumpei Kai, Shuichi
Hiraoka, Nikki J. Cookson, Eli Zysman-
Colman*, Michael J. Hardie*

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**Homochiral self-sorted and emissive
Ir(III) metallo-cryptophanes**

Homochiral $[\{\text{Ir}(\text{ppy})_2\}_3(\text{L})_2]^{3+}$ metallo-cages are obtained from the assembly of $(\Lambda, \Delta)\text{-}[\text{Ir}(\text{ppy})_2(\text{MeCN})_2]^+$ with racemic cavitand host molecules decorated with pyridyl-ligands (L), and ligand-exchange is observed in solution. Cages are emissive, and small differences in the L-ligands lead to quite distinct emission properties. Ppy = 2-phenylpyridinato.

